

Angle resolved photoemission study of Rh(111)

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I. INTRODUCTION

Transition metal surfaces have been a particular interest caused by their unfilled *d*-band induced phenomena and the importance of catalysts over hydrogenation and reduction reactions¹. In particular, the late transition metals Pt and Rh are known for active catalysts in environmental science as reducing the exhausts, NO_x and CO. In metal surfaces, the 2-dimensional (2-D) Fermi contours have been increasingly interested because they play an important role on the electron-phonon interactions. It may be helpful to understand the surface electronic structure and electron-phonon interaction on Rh(111) surface. And it will help further understand on a catalytic behavior of transition metal surface, which is known for dominantly the charge transfer to the adsorbed reactive gas molecule.

II. RESULTS AND DISCUSSION

We focused on the observation of 2-D Fermi contours and determination of the k_F value. Fig.1 shows a typical ARP spectra collected from the clean Rh(111) and NO/Rh(111) surface along the $\bar{\Gamma}\bar{K}$ symmetry line in the SBZ on Rh(111) surface. The photon energy is $h\nu = 90$ eV. So the free electron final state approximation is proper². The range of surface parallel momentum of initial state is $k = 0 \sim 2.0 \text{ \AA}^{-1}$, which contains hexagonal first SBZ of Rh(111) with $\bar{K} = 1.55 \text{ \AA}^{-1}$ and $\bar{M} = 1.35 \text{ \AA}^{-1}$.

Three surface states of clean Rh(111) surface were identified near the Fermi level within 1 eV by crude test with NO adsorption in Fig. 1. The first is an intrinsic surface state located at binding energy 0.2 eV below E_F and shows almost no dispersion around \bar{K} . This state is labeled S1, and it is very similar to the one of Pt(111). The second is a large *sp*-disperse one labeled S5. This is a surface resonance and it has asymmetry between two $\bar{\Gamma}\bar{M}$ symmetry lines, which is due to the bulk property. The third has a small dispersion near labeled S3 with binding energy 0.3 eV which shows low intensity and is hard to be distinguished clearly. One can see diffusive Fermi contours of Rh(111) made of six-triangular electron pockets centered at \bar{K} and a small asymmetric-hexagon centered at $\bar{\Gamma}$ in Fig. 2. The features are so similar to the ones of Pt(111)³. This image was constructed by the interpolated normalized ARP spectra from the partial portion of the first SBZ area.

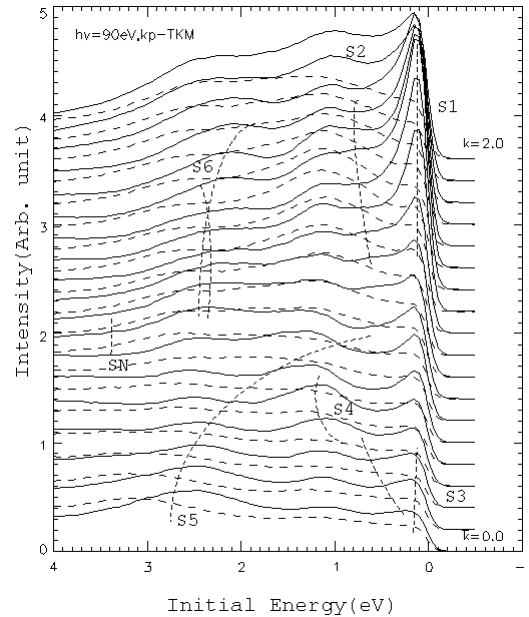


Fig. 1 ARP spectra of clean (solid curves) and NO-covered (dashed curves) Rh(111) collected along the azimuth $\bar{\Gamma}\bar{K}$ at photon energy $h\nu = 90$ eV.

Fig. 2 shows dark semi-hexagon with low intensities near the point and bright triangles with high intensities at the zone boundary of SBZ. It consists of $\Gamma 5$ dominant d -band electron pocket, $\Gamma 6$ closed sp -band dispersion⁴, d -band like X3, X4 hole pockets, and small hole pocket L4. So electron pocket has large Fermi velocity and free-electron like density. It means lower photoemission probability and resulting intensity of the hexagonal area than that of near the zone boundary. Since $\Gamma 5$ sheet is composed of open d -band dominantly and locates near zone boundary, its strong intensity is reasonably assumed due to the localized d -band character at zone boundary and triangle electron pocket. The intensity of surface resonance about $k = 0.8 \text{ \AA}^{-1}$ abruptly increased and it shows asymmetry. Thus the expected hexagon is distorted by bulk electronic structure. On the other hand, the diffusing triangle is composed of the d -band surface states, so it shows very flatness. It is possible to suppose that the valence band of Rh is very similar to that of Pt. It's right to assign the guess based from the paper of Rh(111) surface states. The predicted hole pocket by the rigid band property of Rh near \bar{M} was not observed.

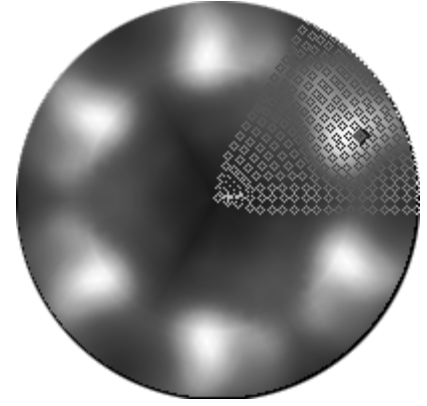


Fig. 2 Fermi edge of clean Rh(111).

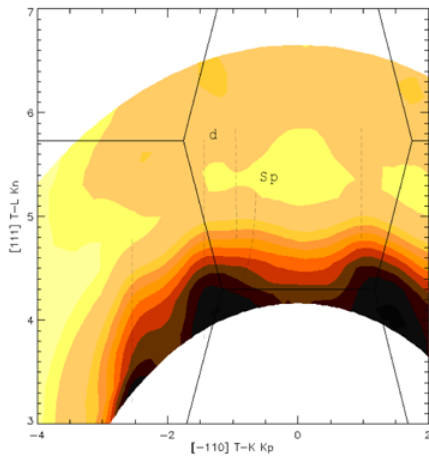


Fig. 3 ARP spectra of constant initial state mode(CIS) for the Fermi level crossing states on Rh(111) along the azimuth $\Gamma\bar{K}$ at photon energy $h\nu = 77 \text{ eV} - 210 \text{ eV}$

Fig. 3 shows k_{\perp} dependence of surface Fermi contours on the high symmetry line of the SBZ. These arcs are the interpolation diagrams of states cross over Fermi edge. It measured ranging from $k = 4.0 \text{ \AA}^{-1}$ to $k = 7.0 \text{ \AA}^{-1}$ and $\Delta k = 0.2 \text{ \AA}^{-1}$. The solid line is the zone boundary of Rh bulk normal to the (111) orientation. If a surface state is an intrinsic, it doesn't depend on k_{\perp} . So it represents as a straight-line strip parallel to the k_{\perp} axis as in Fig. 3. There are two very bright area $k = 4.0 \text{ \AA}^{-1}$ and $\bar{k} = 1.55 \text{ \AA}^{-1}$, $\bar{M} = 1.35 \text{ \AA}^{-1}$ respectively near the zone boundary at crossing area. We can find sp -band that forms a curvature from midpoint about 0.7 \AA^{-1} to 0.9 \AA^{-1} . The surface resonance consisting of hexagonal electron

pocket near zone center looks much nested even if it is free electron-like sp -band $\Gamma 6$. Additionally weak strip footprints independent on k were observed at $k = 0.2 \text{ \AA}^{-1}$ zone center and zone boundary. These are caused by the d -band surface states as reported in the previous theoretical calculation where a surface state near the zone center was flat band. This d -band shows wide hill parallel to the k axis. The large wide dark part of arc plane is due to Cooper minimum of Rh, about $h\nu = 140 \text{ eV}$. From above we determine the 2-D Fermi contours of Rh(111). The hexagonal electron pocket crosses at $k = 0.8 \text{ \AA}^{-1}$ on symmetry line and at $k = 0.7 \text{ \AA}^{-1}$ on symmetry line. The triangular electron pocket crosses at $k = 1.1 \text{ \AA}^{-1}$ on symmetry line. And hole pocket was not observed. But there remains an uncertainty of the k value for the boundary, as much as $\Delta k = 0.1 \text{ \AA}^{-1}$. This may be caused by the hybridization of

d-bands and *sp*-bands on the Fermi surface. It was also observed asymmetry on the \bar{M} point. This is evidence of Rh(111) has fine edge.

III . CONCLUSION

The primary focus of this paper has been the mapping of 2-D Fermi contours on clean Rh(111) with ARPES experiment. Resultant 2-D Fermi contours are much similar to the ones of Pt(111) except the smaller hexagonal electron pocket size. And the flatness of triangular electron pocket is also observed. This flatness of Fermi contours induced by *d*-band and the hybridization of *sp* and *d* band relates the phonon softening of the metal. If Kohn anomaly is observed on Rh(111), it occurs at the twice of observed k_F .

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